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Azo Dyes: From Historical Synthesis to Photoisomerization Applications and Spectral Property Studies

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Abstract. Azo dyes, characterized by the azo group (–N=N–) with sp^2-hybridized nitrogen atoms in a trigonal planar configuration, represent the largest class of industrial dyes (～70% of synthetic dyes). Their versatility arises from the structural diversity of aromatic substituents, enabling tenable optical properties, photoisomerization (first observed by Huntley, 1877), and applications in functional materials. While Johann Peter Griess pioneered diazotization (1858) – the foundational reaction for azo dye synthesis – Paul's synthesis of Congo Red (1875) marked their commercial emergence. However, Miller's 1960 discovery that in vivo enzymatic cleavage of certain azo dyes (e.g., Direct Black 38) releases carcinogenic benzidine led to global bans on dyes containing cleavable carcinogenic aromatic amines. This review covers fundamental chemistry, synthesis, applications, and future prospects of azo compounds.

Keywords: azo dye, photoisomerization, functional materials, synthesis methods

1. Introduction

As its name suggests, azo dye contains the azo group. Both nitrogen atoms are sp^2 hybridized with 1 lone pair each and form a trigonal planar shape. The nitrogen double bond connects to various aromatic derivatives with different substituents. Those functional groups combine together enable structural transformation, color display. the structure of substituents can exhibit various chemical and physical properties which have wide application in functional materials. The azo dyes occupy a large proportion of dyes used in industry (nearly 70%) and of all dyes used (nearly 60%) [1]. The first azo compound and first type of reaction used in synthesis azo compound, the diazotization, is made by Johann Peter Griess in 1858. Azo dyes represent a major class of synthetic dyes. Their development began in 1875 with Paul's successful synthesis of Congo Red. In 1877, Huntley first observed the photoisomerization phenomenon in azo compounds, where their structure undergoes reversible changes upon light exposure. The theoretical foundation for this phenomenon was established in 1909 by Anschütz through his proposed Theory of Photoisomerization.

However, the safety of azo dyes faced a major challenge in 1960. James Miller's research revealed that certain azo dyes (such as Direct Black 38) could be metabolized and decomposed by human intestinal bacteria or enzymes, generating strong carcinogens such as benzidine [2]. This

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discovery directly led to the global ban on the use of azo dyes containing specific carcinogenic aromatic amine structures.

This review will first introduce the basic chemistry of azo compounds, covering their luminescence mechanism, chemical properties, application fields, and common synthesis methods. Finally, the future research and development directions of azo compounds will be discussed.

2. The coloring mechanism of azo dyes

2.1. Molecular origin of color

Animals are able to perceive objects because the photoreceptor cells in their eyes receive light and transmit the signals to the brain for processing, ultimately forming visual images. The colors we perceive fundamentally depend on the characteristics of the incident light. Light is an electromagnetic wave, possessing features such as wavelength, frequency, speed, and energy. For visible light, its wavelength directly determines the colors we see, as shown in Figure 1.

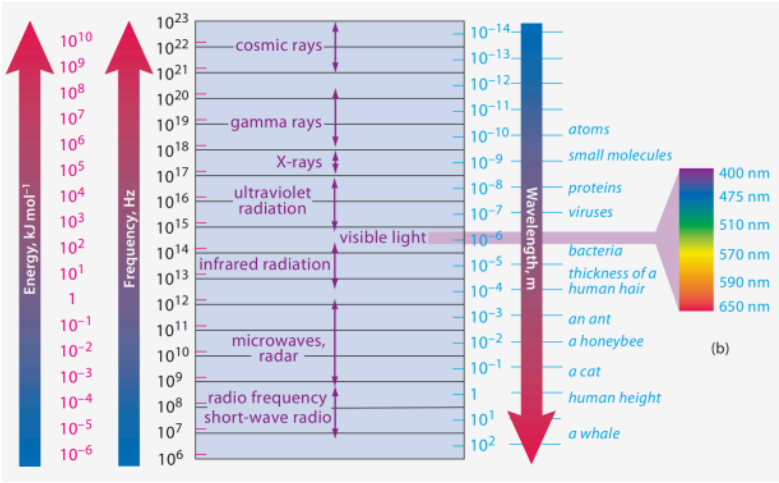


Figure 1. The relationship between wavelength of light and color of light [3]

When light shines on the surface of an object, its perception of color changes. This is because the substance selectively absorbs specific wavelengths of light. The absorption of light by molecules involves the absorption of photon energy. The energy of the absorbed photons must precisely match the energy required for the specific electron transition within the molecule. The unabsorbed light waves are reflected (or transmitted); this reflected light enters our eyes and forms the color we attribute to the object.

For dye molecules, such as azo dyes, the key mechanism by which they absorb visible light and exhibit a specific color usually involves intramolecular π→π transition. This refers to the electron's transition from the bonding π orbital to the higher-energy antibonding π orbital. This transition is particularly important in molecules containing double bonds - especially the azo group (-N=N-) itself is a key double bond - and in molecules with large conjugated systems. A conjugated system is a molecular structure with alternating single and double bonds, allowing electrons to delocalize over a larger area. The size and structure of the conjugated system directly determine the energy required for the π→π* transition: larger and more extended conjugated systems will lower the energy required for the transition (meaning they absorb longer wavelengths of light). Therefore, by designing and modifying the conjugated structure of azo dye molecules, the absorption spectrum of the dye can be precisely controlled, thereby determining its color.

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Conversely, we can analyze which specific wavelengths of light a substance (like a dye) absorbs (i.e., its absorption spectrum) to infer structural features of its molecules, particularly the characteristics of its conjugated system. The method of studying a substance's composition and structure by measuring its interaction with light (absorption or emission) is called spectroscopic analysis.

2.2. Structural factors that change the coloration of azo dyes

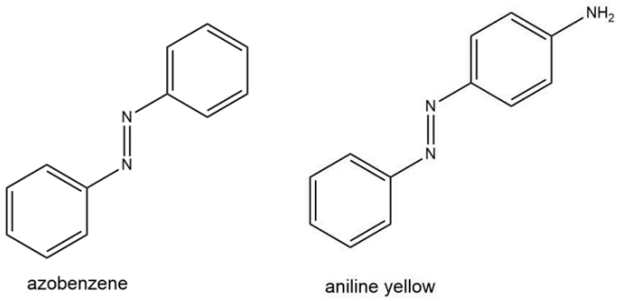


Figure 2. The structure of azobenzene and aniline yellow

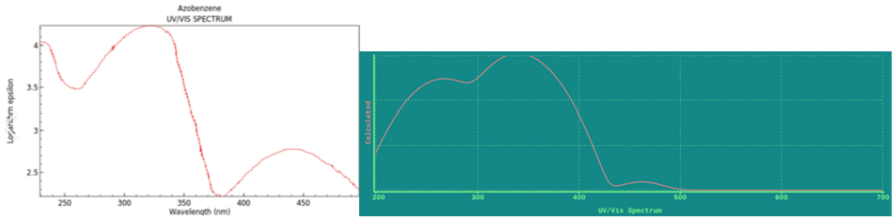


Figure 3. The uv visible spectrum of azobenzene [4] and aniline yellow [5]

from the structural standpoint, we have following azobenzene and aniline yellow. They have the same azo aromatic backbone, the only difference is the amino substituent on the aniline yellow. By comparing the spectrums of azobenzene and aniline yellow on figure 3, we can find a general red shift of curve, resulting the change of colouration from orange to yellow. The substituted aniline has a electron donating group who has a lone pair that can delocalize into the benzene ring. The n→π* transition lower the energy level of electrons of the whole system. Hence the red shift towards the lower frequency.

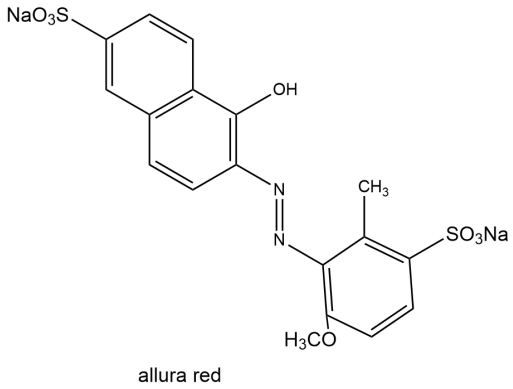


Figure 4. The structure of allura red

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Then if we look at the structure of allura red by observing the substituents on the azo aromatics as figure 4 shown,, there are 1 electron donating substituent hydroxy. However, there are 2 sulfonate groups and 1 COH3 group, all of which intensify the absorbtion peak in the blue color region of the visible spectrum. Therefore enhance the light absorbtion of low frequency. So the colour presented is redder than azobenzene.

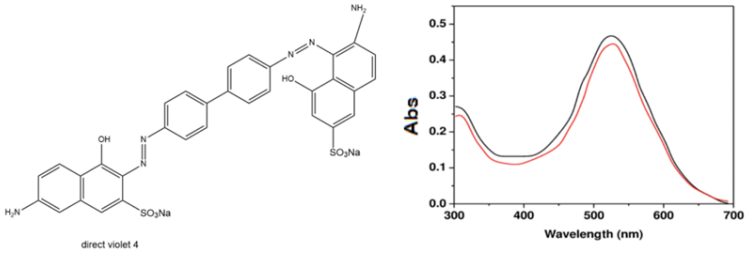


Figure 5. The structure of direct violet 4 and its uv visible spectrum [6]

In the case of direct violet 4, the naphthalene and azo form an extensive conjugated system and also with the addition of lone pair donating group, it highly lowers the energy level of delocalized electrons despite the presence of sulfonate groups as figure 5 shown. In fact, sulfonate groups provide the solubility of the dye. As the final result is, the absorption maxima is highly shifted to the lower frequency. So the color presented is bluer than the rest of the compounds.

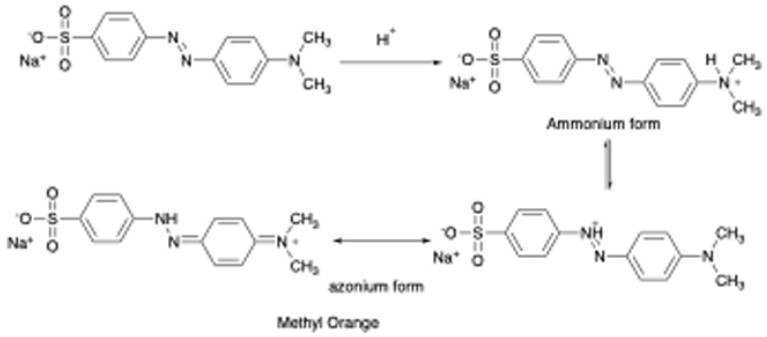


Figure 6. The azonium-ammonium equilibrium of methyl orange in acidic condition

As for methyl orange, a change of coloration from orange to red can be observed in a strong acid medium. As figure 6 shown, the tertiary nitrogen can act as a nucleophile to attack a proton to bear positive charge. Or the lone pair can delocalize into the benzene ring and then transfer over to the beta nitrogen of the azo group. The negative charge bearing nitrogen can be protonated. But in acidic condition, the azonium forms become predominant. The azonium shifts the absorption maxima to higher frequency, so the colour becomes redder.

3. Photoisomerization of the azo bond

Taking azobenzene as an example, this class of compounds exists as two main geometric isomers: the Z-isomer (also known as the cis isomer) and the E-isomer (also known as the trans isomer)as figure 7 shows. Among these, the E-isomer is typically thermodynamically more stable. It possesses a planar structure and features an extended conjugation system (with alternating single and double bonds allowing for electron delocalization), contributing to its relative stability.

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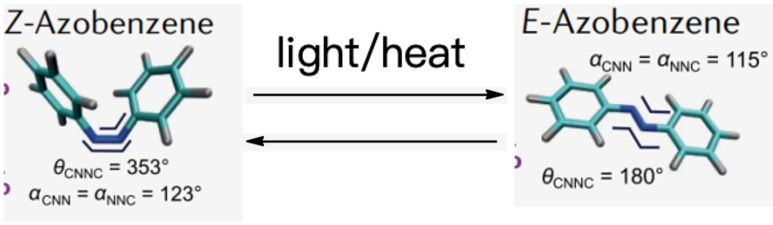


Figure 7. Two isomer of azobenzene [7]

However, when the E-isomer of azobenzene absorbs light of specific wavelengths or is subjected to thermal energy, its structure undergoes a transformation, converting from the E-form to the Z-isomer. Unlike the E-isomer, the Z-isomer generally adopts a non-planar structure (with a twisted conformation), disrupting the conjugation system. Consequently, it is thermodynamically less stable. In the absence of further energy input, the Z-isomer spontaneously reverts back (often slowly) to the more stable E-form.

This reversible conversion process between the E and Z isomers driven by light (or heat) is called photoisomerization. Photoisomerization leads to significant changes in the molecular spatial configuration (from planar to non-planar) and electronic structure (altering the degree of conjugation). Therefore, we can utilize this unique property to precisely control the three-dimensional shape of compounds, photophysical properties (such as absorption/emission spectra), and other related characteristics. This capability provides a key approach for designing intelligent functional materials (such as optical switches, molecular machines, and data storage materials).

4. Applications of optical isomerization

4.1. Light-controlled molecular filter

The photo-isomerization property of azobenzene (such as -N=N-) makes it possible to design intelligent molecular filtering materials. By inducing a reversible switch between the planar trans (E) configuration and the twisted cis (Z) configuration through light, the spatial extension degree of the connecting groups can be precisely controlled. This length modulation directly determines the pore size inside the material: the E configuration reduces the pore size, while the Z configuration enlarges it. By selectively controlling the pore size through light, it is helpful for efficient screening of target molecules and achieving light-driven compound separation and filtration, as shown in Figure 8.

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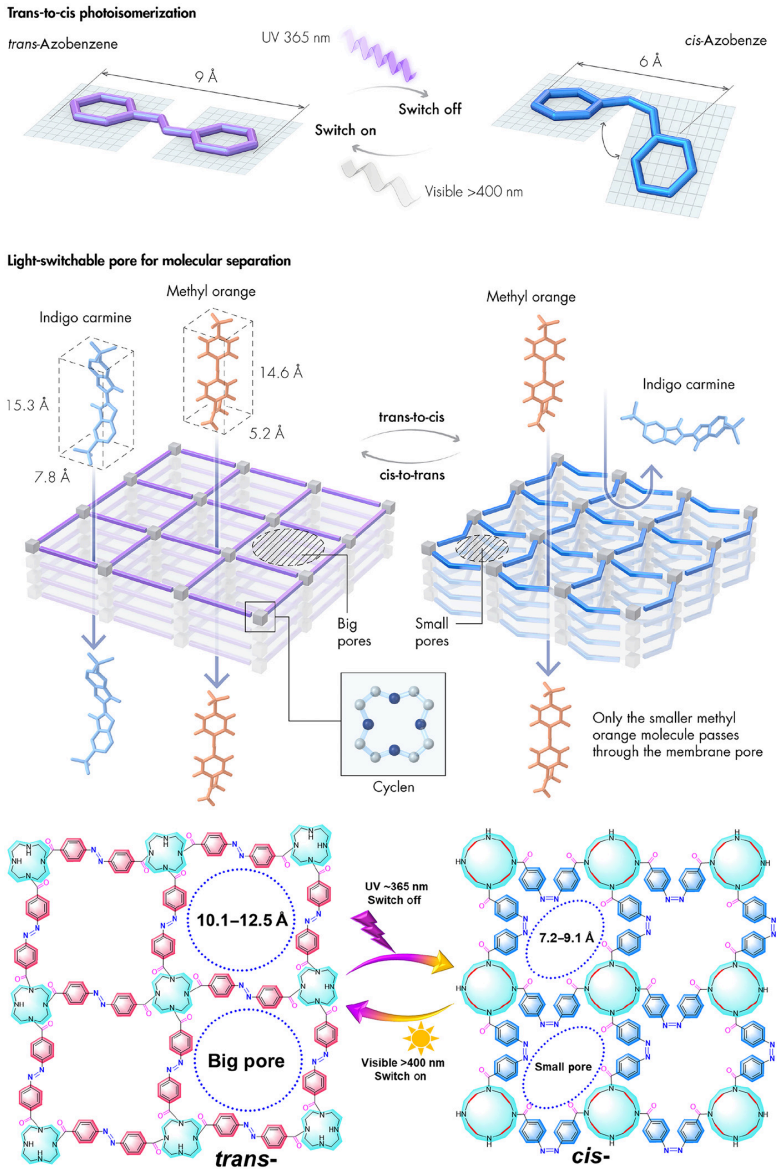


Figure 8. Functional schematic of the azide bond network [8]

4.2. Light-triggered drug delivery system

Introducing the azo bond (-N=N-) into the framework of the drug carrier can enable precise drug release through photo-isomerization. The photo-triggered E→Z transformation alters the chemical polarity (such as hydrophilicity/hydrophobicity) and three-dimensional conformation of the carrier. These controlled changes disrupt the interaction between the carrier and the drug or open molecular "doors", thereby achieving on-demand drug release and promoting the development of targeted therapy.

4.3. Light switch catalyst

By taking advantage of the photo-responsive property of azobenzene, photo-regulated catalysts can be designed. When the catalytic active sites are functionalized with azo groups, the photo-driven E/Z isomerization can reversibly regulate their spatial geometric structure and electronic environment.

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This dynamic control can activate or deactivate the catalytic center by light, thereby achieving direct optical regulation of the initiation/termination of chemical reactions and serving sustainable synthesis.

5. Synthesis methods of azo compounds

5.1. Nitration/coupling reaction

There are mainly two pathways for constructing the characteristic N=N double bond of the azo group: the diazotization/coupling sequence, or through the oxidation or reduction of nitro, nitroso or aniline derivatives.

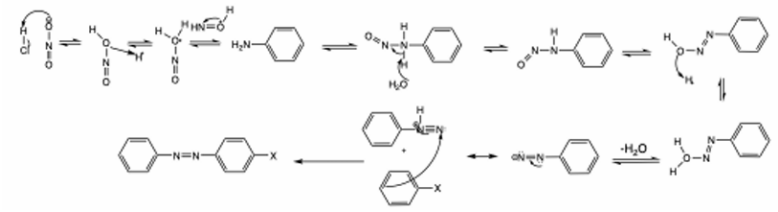


Figure 9. The diazotization and coupling reactions

As shown in Figure 9, the formation of azo compounds begins with the conversion of aniline into a diazonium salt, followed by a coupling reaction with an activated aromatic ring. The diazonium salt is synthesized in situ using a mixture of nitrous acid and hydrochloric acid. During this process, the nitrous acid reacts with hydrochloric acid to form nitroxide species. This electrophilic reagent is attacked by the nucleophilic nitrogen atom in aniline. Subsequently, the protonation of the nitroxide oxygen leads to its elimination in the form of a water molecule. The resulting positive charge is stabilized by forming a double bond between the two nitrogen atoms, generating a diazonium cation with a chloride ion as the counterion. This diazotization step is carried out at 0°C to minimize contact with water, as the diazonium salt is prone to decomposition and releases nitrogen gas.

The subsequent coupling reaction proceeds via an electrophilic aromatic substitution mechanism. The reaction requires an electron-rich aromatic ring, typically activated by an electron-donating group. This directing group guides the diazonium electrophile to the para position; if this site is blocked, substitution occurs at the ortho position. It is noteworthy that when the coupling partner is an alkyl-substituted ring, the diazonium electrophile itself must bear an electron-withdrawing group to facilitate the reaction.

5.2. Oxidation

Developing green and efficient synthetic routes for aromatic azo compounds is a major focus in chemistry. Over the past decade, transition metal compounds have garnered significant interest due to their variable oxidation states and redox properties. These catalysts can utilize oxygen to directly oxidize aromatic anilines, forming azo compounds. This approach is highly attractive from a green chemistry perspective, as molecular oxygen is an ideal, atom-economical oxidant. For instance, mesoporous manganese oxide materials, using air as the terminal oxidant, can convert various aniline derivatives into their corresponding azo compounds [9].

The development of solvent-free reactions is another attractive research goal. Using copper acetate catalyzed by a small amount of a palladium salt, anilines can be rapidly converted to aromatic azo compounds under base-free and solvent-free conditions [10]. This method offers a

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green route for synthesizing both symmetric and asymmetric aromatic azo compounds and highlights the potential of transition metal catalysts.

A key challenge in the direct oxidation of aromatic amines is controlling the oxidation state. Catalytic oxidation often leads to a mixture of by-products, including nitrobenzene, azoxybenzene, and azobenzene, with the product distribution being highly dependent on the catalyst's performance. While direct oxidation has many advantages, over-oxidation can sometimes lead to low selectivity and numerous by-products. Furthermore, some oxidants are not practical for large-scale industrial applications.

5.3. Reduction

Aromatic amines are commonly derived from the reduction of aromatic nitro compounds. Therefore, a one-step synthesis of aromatic azo compounds directly from nitroaromatics would be highly efficient and environmentally friendly. Mondal et al. reported the use of a nanoscale organic cage as a template to prepare gold nanoparticles (AuNPs). These supported AuNPs functioned as a heterogeneous photocatalyst, selectively reducing nitroaromatics with 2-propanol to produce the corresponding azo compounds in high yield at room temperature [11].

New functional materials like boron nitride (BN) are gaining traction in catalysis. Hexagonal boron nitride (h-BN) is a two-dimensional, layered material with low toxicity and high thermal stability, similar to graphene. As a catalyst support, h-BN provides a platform that can enhance the reactivity of metal nanoparticles. Liu et al. synthesized gold nanoparticles supported on h-BN nanoplates [12]. This composite catalyst selectively converts nitrobenzene to azobenzene or its hydrogenated derivative using isopropyl alcohol and KOH, under either nitrogen or air.

Despite their excellent activity, the high cost of noble metal nanoparticles limits their widespread use. Consequently, cheaper transition metal catalysts are of great interest. Pahalagedara et al. developed a sea urchin-like nickel/graphene nanocomposite that uses hydrazine to selectively reduce substituted nitroaromatics to azo compounds; this magnetic catalyst was also easily recovered and reused [13].

Copper is a more abundant, cheaper, and easier-to-handle alternative. Moran et al. described efficient copper nanoparticles that catalyze the controlled hydrogenation of nitroaromatics to azo compounds using different hydrogen donors [14]. A key finding was that the hydrogen source dictates the product; for example, using ethanolamine afforded azobenzene with 96% selectivity. This method provided azo derivatives with an average yield of 85%.

Molecular hydrogen is undoubtedly a green and cost-effective hydrogen source for industrial-scale reductions. Hu et al. reported a worm-like palladium nanomaterial that catalyzes the conversion of nitroaromatics to azo compounds under mild conditions. This catalyst, with a narrow size distribution around 3.5 nm, reduces nitrobenzene to azobenzene using H_2 in the presence of a base, but produces aniline in the absence of a base [15].

Huang et al. prepared a cobalt/nitrogen-doped carbon catalyst for the selective reduction of nitroaromatics to either anilines or azo compounds using H_2, with the product determined by the reaction's basicity [16]. The hydrogenation pathway involves nitrosobenzene and N-phenylhydroxylamine intermediates, ultimately leading to aniline. Under basic conditions, however, the pathway shifts: the condensation between N-phenylhydroxylamine and nitrosobenzene is favored, producing azoxybenzene, while the further reduction to aniline is suppressed.

While the reductive coupling of nitroaromatics is generally more efficient than the oxidative coupling of amines, the frequent reliance on costly catalysts can limit its practical application.

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5.4. Biochemical methods

A core principle of biochemical synthesis is using enzymes as catalysts to drive highly efficient and selective reactions, thereby reducing energy consumption and environmental pollution. Sousa et al. described the synthesis of azo compounds via laccase-catalyzed oxidative coupling of aromatic amines under mild conditions [17]. The mechanism involves enzyme-mediated aerobic oxidation of the amine to an unstable aminyl cation radical, which deprotonates to a neutral radical. Coupling of two radicals forms a hydrazo intermediate, which is then dehydrogenated to yield the azo compound. A notable drawback is that substrates with electron-withdrawing groups can generate unstable radical intermediates, leading to lower yields.

Pariyar et al. utilized ethyl lactate as a green solvent for a one-pot synthesis of symmetrical and asymmetrical aromatic azo compounds from amines [18]. In this catalyst-free system, ethyl lactate acts as an effective mediator, where aniline is oxidized by potassium peroxomonosulfate to nitrosobenzene. A second aniline molecule then attacks the nitrosobenzene, followed by dehydration to yield trans-azobenzene. The primary advantage of this method is its use of an environmentally benign solvent that mimics enzyme function. However, the mechanism is not fully elucidated, and the method is currently not applicable for synthesizing asymmetric azo compounds.

6. Conclusion

Azo compounds, dominated by the structurally versatile azo group (-N=N-), form the largest class of industrial synthetic dyes (～70% market share), with their optical and functional properties exquisitely tunable through aromatic substituent design. However, historical safety concerns—specifically the enzymatic release of carcinogenic aromatic amines (e.g., benzidine)—necessitated stringent regulations, driving research toward safer alternatives. Central to their modern value is photoisomerization: the light-triggered reversible transition between planar E and bent Z isomers enables dynamic control over molecular conformation and electronic states. This unique mechanism underpins breakthroughs in functional materials, including optical filters (light-gated pore-size modulation), targeted drug delivery systems (stimuli-responsive carrier polarity shifts), and photocatalysts (spatiotemporal reaction control). Concurrently, synthesis methodologies have evolved toward green and efficient paradigms. While diazotization/coupling remains fundamental, emerging strategies prioritize atom economy—such as aerobic oxidation of anilines catalyzed by transition metals (e.g., MnO_x, Cu/Pd)—and step reduction via nano-catalysts (e.g., Au cages, Co-N-C) under mild conditions. Challenges persist in selectivity control and catalyst cost, motivating biocatalytic routes (e.g., laccase-mediated coupling) and enzyme-mimetic systems. Future advancement hinges on multidisciplinary convergence: (1) designing non-cleavable azo scaffolds to eliminate toxicity risks; (2) engineering low-cost robust catalysts (e.g., non-noble metal hybrids); (3) integrating photoisomerization with nanotechnology for adaptive devices; (4) leveraging computational tools to predict properties. Thus, azo chemistry transcends traditional dye applications, poised to enable sustainable, intelligent material platforms through synergistic innovation.

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All the authors contributed equally to this work and should be considered as co-first author.

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